



Synthesis of polylactic acid by direct polycondensation under vacuum without catalysts, solvents and initiators

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ABSTRACT

In order to reduce the production cost of polylactic acid (PLA), L-lactic acid was polymerized by direct polycondensation (DP) under vacuum without catalysts, solvents and initiators. Experiments were conducted at polymerization temperatures (T_p) of 150–250 °C. The maximum PLA molecular weight obtained was 90 kDa at 200 °C after 89 h under vacuum. Above 200 °C, PLA is thermally degraded by specific scission. The DP activation energy (E_a) was also investigated and was found to be larger than that required by catalyzed ring opening polymerization (ROP). Furthermore, the E_a was higher than the deactivation energy (E_d) for both DP and ROP. PLA yields were higher at lower T_p , while the yield of lactide increased with T_p . The total yield of PLA and lactide was approximately 52–75 wt.%. The uncatalyzed DP method may have applications in on-site cell plant production, where compactness is required, as well as safe and simple operating procedures.

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1. Introduction

Recently, the demand for plastics made from biomass (bioplastics) has increased because they can reduce environmental carbon dioxide emissions, which induces global warming, and their production does not require fossil fuel resources, thus reducing the environmental load required to produce these plastics. If bioplastics are going to be able to address the issues of global warming or fossil fuel use, they will need to be used in large quantities. However, the use of bio-plastics remains limited because their production costs are 3–10 times higher than those of conventional plastics [1].

Poly(lactic acid) (PLA) derived from biomass is a typical bio-plastic that can be made in a three-step process of fermentation, separation and polymerization. Nature Works Co. (USA) has produced PLA from recombinant corn by means of an intensive large-scale process that reduces production costs [2].

In an attempt to further reduce the cost of producing PLA, we proposed an on-site cell plant method for all three processes. For the fermentation process, L-lactic acid was fermented using fresh cassava root (FCR) as the substrate and concentrate of maguro waste (CMW) and tofu liquid waste (TLW) as the medium, without saccharification and *Streptococcus bovis* as the bacterial strain [1,3,4]. The polymerization process used to synthesize PLA was direct polycondensation (DP) under vacuum without catalysts, solvents and

initiators. This process fulfills the conditions of compactness, as well as safe and simple operation for an on-site cell plant concept.

PLA is typically synthesized by ring opening polymerization (ROP) of lactide, a process that uses catalysts such as tin, zinc, aluminum and lead, initiators such as *n*-, *sec*- and *tert*-butyl lithium, and solvents such as diphenyl ether, toluene and chloroform. Many of these components are toxic or flammable. As a result, this process requires purification to remove the unwanted materials from the product, which requires complex facilities [5,6].

This paper reports the synthesis of PLA by DP without catalysts, solvents and initiators by varying the T_p from 150 to 250 °C and the pressure from atmosphere pressure to vacuum for 96 h, in accordance with the specifications for on-site cell plants. The properties of the PLA synthesized by DP were compared with those of PLA synthesized by ROP.

2. Materials and methods

2.1. Materials

L-Lactic acid (L-LA: special grade) was supplied by Wako Pure Chemical Industries, Ltd. (Tokyo, Japan) with a monomer concentration of 60 wt.%, a total acidity of 90 wt.% and a density of 1.224 kg/L. Chloroform (Wako Pure Chemical Industries, Ltd. (Tokyo, Japan)) was used as the eluent in gel permeation chromatography (GPC). The polystyrene standard for GPC calibration and the lactide standard for FTIR analyses were supplied by Sigma-Aldrich Chemical Co. (USA). We used PLA produced by Lecea Mitsui Chemicals Inc. (Japan) as a standard.

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Nomenclature

[A] ₀	initial concentration of the –COOH or –OH group [mol L ⁻¹]
[A]	concentration of the –COOH group [mol L ⁻¹]
[B]	concentration of cyclic monomer B, e.g., lactide [mol L ⁻¹]
[B] ₀	initial concentration of cyclic monomer B [mol L ⁻¹]
[Cat]	catalyst concentration [mol L ⁻¹]
E _a	activation energy of polymerization [kJ mol ⁻¹]
E _d	deactivation energy of thermal degradation [kJ mol ⁻¹]
k ₁	first order rate constant for ROP polymerizations of lactide [min ⁻¹]
k ₋₁	first order rate constant for thermal degradation in ROP polymerizations of lactide [min ⁻¹]
k _{app} ^R	apparent rate constant of polymerization for ROP [L mol ⁻¹ min ⁻¹]
k _{-app} ^R	apparent rate constant of thermal degradation for ROP [min ⁻¹]
k ₂	second order rate constant of polymerization for DP [L mol ⁻¹ min ⁻¹]
k _{2app} ^D	apparent polymerization rate constant for DP [min ⁻¹]
k _{2-app} ^D	apparent rate constant of thermal degradation for DP [min ⁻¹]
k ₃	third order rate constant of polymerization for DP [L ² mol ⁻² min ⁻²]
Mn	number average molecular weight [g/mol]
Mw	weight average molecular weight [g/mol]
n	degree of polymerization in stepwise polymerization
P	degree polymerization in ring opening polymerization
t	Time [min]
T	Temperature [°C], [K]
ω	initial monomer concentration of L-LA [wt.%]
ρ	Density [kg/L]

2.2. Apparatus and procedures

Fig. 1 shows the experimental apparatus used for polymerizations. Polymerizations were conducted in a 1 L four-necked separable flask equipped with a mechanical stirrer and a reflux condenser connected to an inline cold trap and a vacuum pump. Thermocouples were used to measure the internal and exterior temperatures of the solution in the reactor and the exterior of the flask. To control the internal and exterior temperatures of the reactor, main and sub-heaters were installed surrounding the reactor. The reactor pressure was measured by a transducer and monitored by a computer. The pressure in the reactor was lowered incrementally using a vacuum pump.

Two hundred grams of L-LA was added to the flask, and PLA was synthesized by direct polycondensation (DP) through three operations: distillation, oligomerization and polymerization. The temperature and pressure during the polymerization were precisely controlled.

First, during the distillation period, L-LA was heated to the distillation temperature (*T_d*) of 150 °C, after which the temperature was maintained at the *T_d* for 150 min at atmosphere pressure. This was followed by the oligomerization period, which lasted between 150 and 300 min. The temperature and pressure were then brought to the polymerization temperature (*T_p*) and vacuum, respectively. The

pressure was reduced incrementally to 10 mmHg over five 30 min periods. The distillate was removed from the condenser trap and measured every 30 min. Then, during the polymerization period, the L-LA was polymerized at various polymerization temperatures (*T_p*) between 150 and 250 °C at 10 mmHg for 96 h. Samples were taken from the reactor and the trap at 12 h intervals. At the end of the reaction, the products were poured into a Petri dish and allowed to cool to room temperature.

2.3. Analytical method

The concentrations of the L-LA monomer in the reactor and trap were analyzed by a biosensor equipped with an auto sampler (BF-5: Oji Scientific Instruments, Osaka). The total acidity in the L-LA solution was analyzed to determine the oligomer concentration, as calculated by an acid–base titration method (JIS K8726). The amount of oligomer present was calculated from the difference between the amount of monomer and the total acidity. The PLA's weight average molecular weight (Mw), number average molecular weight (Mn) and Mw/Mn ratio were determined using a gel permeation chromatography (GPC) system equipped with two chromatography columns (Shodex K803 and Shodex K804) and a RI detector. Chloroform was used as the eluent at a flow rate of 1 mL/min, and the molecular weights were calibrated to a polystyrene standard at 40 °C. The functional groups of PLA, lactide and L-LA were analyzed by Fourier Transform Infrared Spectroscopy (FTIR: JASCO FT/IR-4100ST).

3. Basic considerations

3.1. The rate of stepwise polymerization

a. Self-catalyzed polymerization

In the absence of an exogenous strong acid, the acid monomer acts as its own catalyst in the esterification reaction. The condensation can be expected to be third order overall in the concentration of the –OH and –COOH (or A) functional groups [7,8]:

$$\frac{d[A]}{dt} = -k_3 \cdot [-OH] \cdot [A]^2, \quad (1)$$

where *k₃* is the rate constant of the third order reaction, and [–OH] and [A] are the concentrations of –OH and A groups, respectively.

Since there is one –OH group for each –COOH group, the equation can be written as:

$$\frac{d[A]}{dt} = -k_3 \cdot [A]^3. \quad (2)$$

Integration of Eq. (2) yields:

$$\frac{[A]_0^2}{[A]^2} - 1 = 2[A]_0^2 \cdot k_3 \cdot t. \quad (3)$$

However, the degree of polymerization (*n*) in a stepwise polymerization can be expressed by Eq. (4) (assuming no mass is lost):

$$n = \frac{[A]_0}{[A]}. \quad (4)$$

Thus, Eq. (3) can be simplified to:

$$n^2 - 1 = 2[A]_0^2 \cdot k_3 \cdot t. \quad (5)$$

Eq. (5) makes clear that the relationship between (*n*² – 1) and *t* should be linear if the polymerization follows this model of self-catalyzed polymerization.

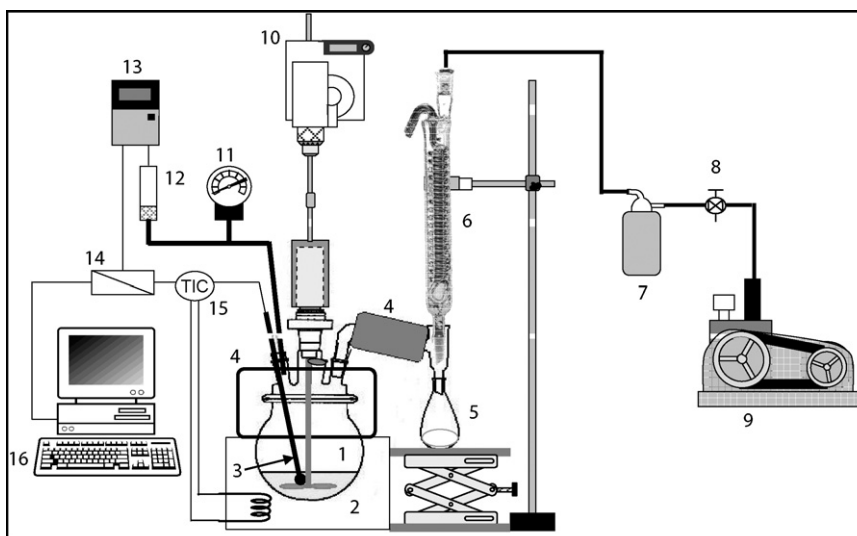


Fig. 1. The experimental apparatus for PLA polymerization. (1) Four-necked separable flask, (2) main-heater, (3) thermocouple, (4) sub-heater, (5) condensate trap, (6) condenser, (7) cold trap, (8) control valve, (9) vacuum pump, (10) stirrer, (11) pressure gauge, (12) transducer, (13) amplifier, (14) A/D converter, (15) temperature indicating controller (TIC), and (16) personal computer.

b. External catalysis of polymerization

The stepwise polymerization involving an external catalyst follows the second order reaction [7,8]:

$$\frac{d[A]}{dt} = -k_2 \cdot [-OH] \cdot [A], \quad (6)$$

where k_2 is the rate constant of the second order reaction. Setting $[-OH] = [A]$ gives:

$$\frac{d[A]}{dt} = -k_2 \cdot [A]^2. \quad (7)$$

Integration of Eq. (7) gives:

$$\frac{[A]_0}{[A]} - 1 = [A]_0 \cdot k_2 \cdot t. \quad (8)$$

Combining Eq. (4) and Eq. (8) yields:

$$n - 1 = [A]_0 \cdot k_2 \cdot t. \quad (9)$$

Eq. (9) shows that the relationship between $(n - 1)$ and t should be linear if the polymerization follows this model of external catalysis. We define the apparent polymerization rate constant k_{2app}^D as shown in Eq. (10):

$$k_{2app}^D = k_2 \cdot [A]_0. \quad (10)$$

Substituting Eq. (10) into Eq. (9) yields:

$$n - 1 = k_{2app}^D \cdot t. \quad (11)$$

3.2. The rate of ring opening polymerization

The ring opening polymerization (ROP) reaction is a first order reaction [9–11], thus:

$$\frac{d[B]}{dt} = -k_1 \cdot [B], \quad (12)$$

where $[B]$ is the concentration of cyclic monomer and k_1 is the first order rate constant for the reaction. We obtain Eq. (13) by integrating Eq. (12):

$$\ln \frac{[B]_0}{[B]} = k_1 \cdot t, \quad (13)$$

where $[B]_0$ is the initial concentration of cyclic monomer B.

On the other hand, the coefficient k_1 is proportional to the concentration of the catalyst in ROP, that is:

$$k_1 = k_{app}^R \cdot [Cat], \quad (14)$$

where k_{app}^R is the apparent rate constant of polymerization for ROP and $[Cat]$ is the catalyst concentration.

Inserting the coefficient k_1 into Eq. (12) yields:

$$\frac{d[B]}{dt} = -k_{app}^R \cdot [B][Cat]. \quad (15)$$

3.3. The rate of the polymer's thermal degradation by the catalyst

The rate of the polymer's thermal degradation in the presence of a catalyst is given by Eq. (16) [12]:

$$\frac{dP}{dt} = -k_{-1} \cdot P, \quad (16)$$

where k_{-1} is the rate constant for thermal degradation and P is the degree of polymerization.

The coefficient k_{-1} is proportional to the catalyst concentration, that is:

$$k_{-1} = k_{-app}^R \cdot [Cat], \quad (17)$$

where k_{-app}^R is the apparent rate constant of thermal degradation by the catalyst.

Inserting the coefficient k_{-1} into Eq. (16) yields Eq. (18):

$$\frac{dP}{dt} = -k_{-app}^R \cdot P \cdot [Cat]. \quad (18)$$

Thus, the rate of the thermal degradation reaction in the presence of a catalyst is the same as the rate of ROP polymerization.

4. Results and discussion

4.1. Impact of temperature and pressure on total condensate during the distillation and oligomerization periods

Fig. 2 shows the temperature and pressure in the reactor (a) and the total condensate removed (b) at various polymerization temperatures (T_p) and pressures over 300 min in the distillation and oligomerization periods. At about 45 min, a second order phase transition occurred at $128 \pm 2^\circ\text{C}$ in the reactant (point P in Fig. 2a),

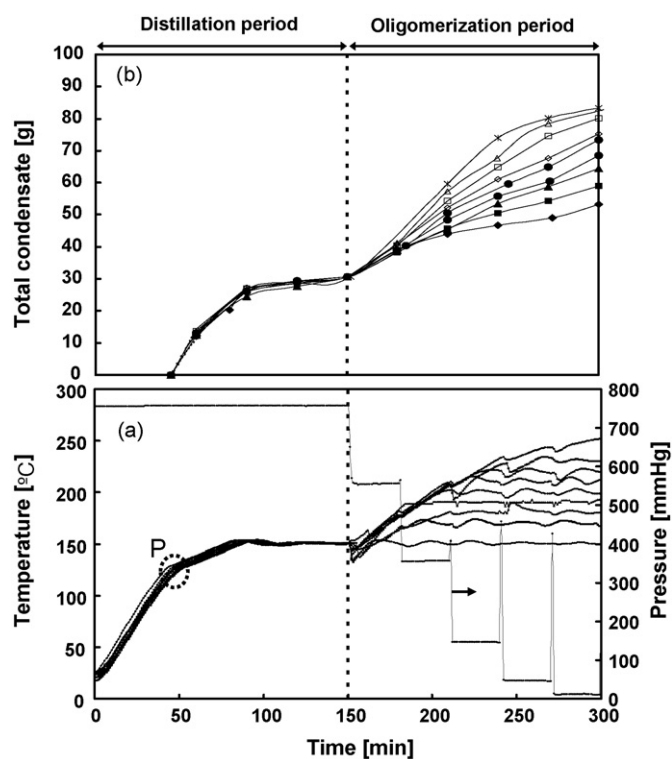


Fig. 2. The temperature and pressure in the reactor (a) and total condensate removed (b) during the distillation and oligomerization periods. At following polymerization temperature 150 °C (◆), 170 °C (■), 180 °C (▲), 190 °C (●), 200 °C (○), 210 °C (◇), 220 °C (□), 230 °C (△), 250 °C (*).

where heat was constantly supplied until 150 °C was reached and the total acidity of the L-LA increased to about 100 wt.% from 90 wt.% by distillation. The amounts of water, monomer and oligomer in the reactor and condensate were in agreement with the diagram by Vickroy [13]. At about 90 min, the reactor temperature reached the specified distillation temperature T_d of 150 °C, which was maintained throughout the distillation period until 150 min had elapsed. The temperature and pressure conditions throughout the distillation period were the same for all trials.

The total condensate was measured as the condensate in the trap and the condensate adhering to the walls of the flask and condenser.

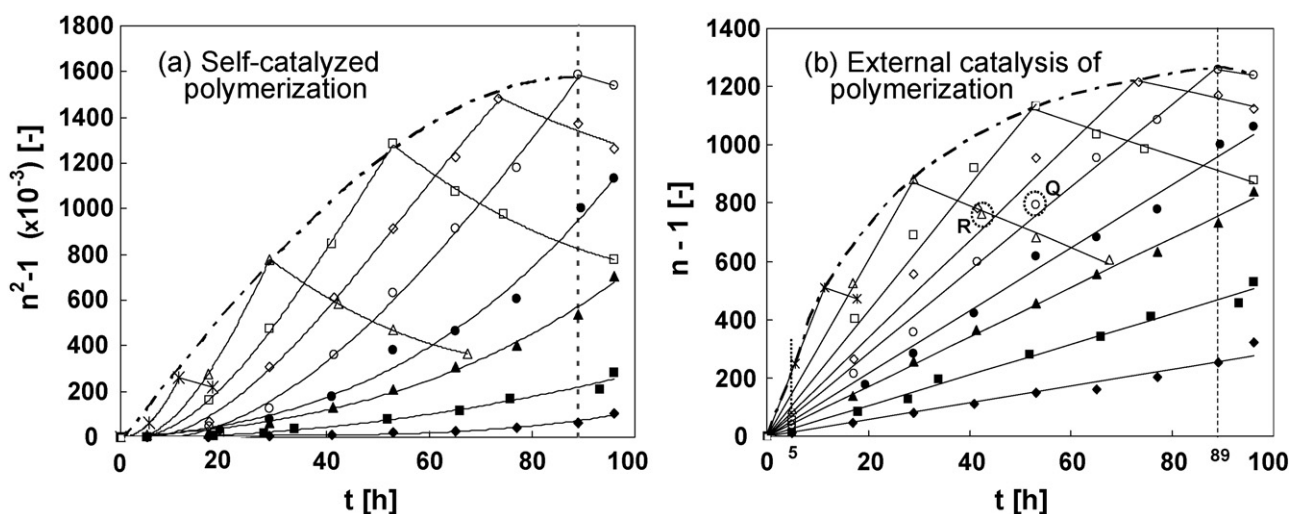


Fig. 3. The effect of polymerization time (t) on the degree of PLA polymerization (n). Symbols: 150 °C (◆), 170 °C (■), 180 °C (▲), 190 °C (●), 200 °C (○), 210 °C (◇), 220 °C (□), 230 °C (△), 250 °C (*).

The condensate on the walls of the flask and in the condenser was preliminarily measured to weigh 6.0 g. During the oligomerization period (150 min < t < 300 min), the total condensate increased as a result of the incremental reduction in pressure. During the polymerization period, the temperature and pressure were kept constant at T_p and 10 mmHg from 300 min to 96 h.

4.2. The rate of polymerization and thermal degradation

Fig. 3 shows the effect of polymerization time (t) on the degree of polymerization of the polylactic acid (n) at various polymerization temperatures (T_p) between 150 and 250 °C. For the self-catalyzed polymerization with third order kinetics, the relationship between $(n^2 - 1)$ and t is shown in Fig. 3a, while the plot of the second order reaction using an external catalyst is shown in Fig. 3b. The experimental results support the model of an externally catalyzed polymerization, since $(n - 1)$ and t have a linear relationship (Fig. 3b) from Eq. (11). That is, the reaction mechanism for L-LA polymerization by uncatalyzed DP, is overall second order, because L-LA is a strong acid that acts as a catalyst during polymerization, in spite of the large amount of mass lost under these conditions.

The rate coefficient $k_{2,app}^D$ in Eq. (11) was obtained from the slope of the graph in Fig. 3b, while the coefficient k_2 was calculated from Eq. (10).

We also compared the polymerization rate constant for DP with that of ring opening polymerization (ROP). The polymerization rate for ROP is represented by Eq. (15), and the coefficient k_{app}^R is an apparent second order reaction rate constant, in which the terms that appear in the rate law are the concentrations of lactide and catalyst. The polymerization rate constants k_2 and k_{app}^R have the same dimension [$L \text{ mol}^{-1} \text{ min}^{-1}$].

At $T_p = 200$ °C, the degree of PLA polymerization (n) reached 1260 at 89 h and decreased after that point. At high temperatures, PLA is in equilibrium with radical lactide by radical homolysis pathways [14]. Since the melting point of lactide is 94–96 °C, lactide is vaporized at high temperatures and low pressures, and is then trapped by the condenser. As thermal degradation takes place and lactide is distilled, PLA shifts to a lower molecular weight. PLA's equilibrium with radical lactide depends on the temperature. Thermal degradation was found to occur at 200 °C when no catalyst is present. Higher temperatures lead to faster and more prevalent thermal degradation. For example, at $T_p = 250$ °C, the degree of polymerization is about 509 after 10 h. The boundary where polymerization and ther-

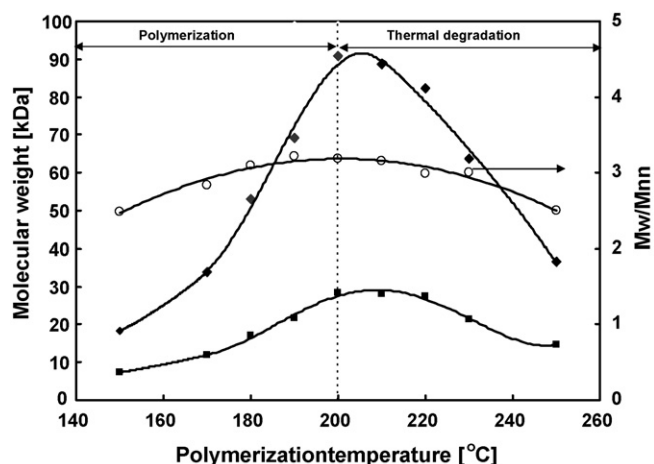


Fig. 4. The effects of polymerization temperature on the PLA's molecular weight and Mw/Mn. Symbols: Mw (\blacklozenge), Mn (\blacksquare), ratio Mw/Mn (\circ); at $T_p \leq 200^\circ\text{C}$ for $t = 89$ h, at $T_p > 200^\circ\text{C}$ for $t = \text{maximum molecular weight}$.

mal degradation occur simultaneously is shown by the dashed line in Fig. 3b.

This study evaluated the rate of thermal degradation by representing the experimental reaction rate constant ($k_{2\text{-app}}^D$) for the uncatalyzed thermal degradation as:

$$n - 1 = k_{2\text{-app}}^D \cdot t + b. \quad (19)$$

However, Okamoto and Matsuo [12] studied the catalyzed thermal degradation of PLA and proposed the rate law shown in Eq. (16). The coefficient k_{-1} is the first order rate constant for thermal degradation in the presence of a catalyst. The thermal degradation rate constants $k_{2\text{-app}}^D$ and k_{-1} have the same dimensions [min^{-1}].

Fig. 4 shows the effects of polymerization temperature (T_p) on the weight average molecular weight (Mw), the number average molecular weight (Mn) and the PLA's Mw/Mn ratio. For $T_p < 200^\circ\text{C}$, Mw and Mn are the molecular weights at $t = 89$ h, the time when the PLA reached its maximum molecular weight (90 kDa) at $T_p = 200^\circ\text{C}$ (in Fig. 3b) and for $T_p > 200^\circ\text{C}$, the Mw and Mn parameters are the maximum values allowed by thermal degradation.

Harse et al. [15] studied the synthesis of PLA from L-LA by DP and found that the PLA reached a maximum Mw of 7 kDa using SnCl_2 as the catalyst and a Mw of 2.35 kDa without a catalyst at 180°C after 24 h under nitrogen atmosphere. Kaitian et al. [16] reported a maximum Mw of 6 kDa for D,L-PLA synthesized by uncatalyzed and solvent-free DP at 200°C for 24 h under nitrogen atmosphere. Low Mw polymers resulted due to difficulties in removing water from the bulk polymerization. Ajioka et al. [17] have reported the polymerization of L-LA by DP using a Sn catalyst and diphenyl ether as the solvent. High MW PLA (240 kDa) was produced after 24 h at 130°C . In the presence of a catalyst and solvent, the small amount of water remaining in the reaction mixture can be removed azeotropically at a relatively low temperature under high vacuum. However, such a process requires multiple reactors, complex facilities and a purification step to remove the catalyst and the solvent from the product [6].

Commercially available PLA, such as that produced by Nature Works, is synthesized from lactide by ROP using a tin octoate catalyst at $180\text{--}210^\circ\text{C}$ for 5 h. The Mw of the PLA produced is 111–145 kDa [18]. Using the same method, Ajioka et al. [17] reported the polymerization of L-Lactide by ROP using tin octoate as the catalyst and 1-dodecanol as the solvent. This procedure produced high MW PLA (430 kDa) after 5 h at 200°C . While the Mw of PLA obtained by our present conditions is lower than that obtained

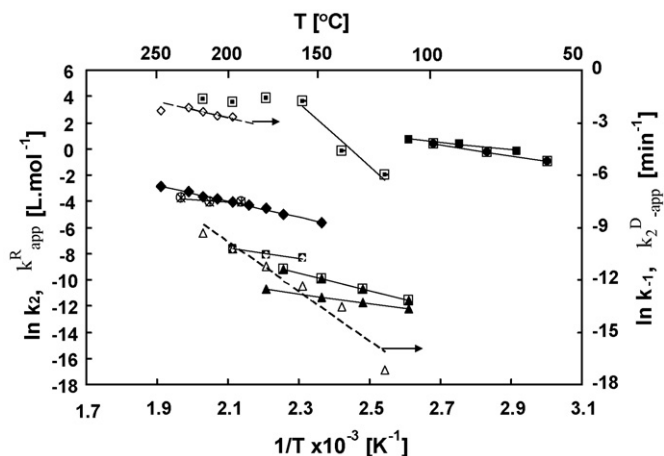


Fig. 5. Arrhenius plot for the polymerization and thermal degradation of polylactic acid. Symbols: Polymerization (\blacklozenge), and thermal degradation (\diamond) by present work, Kaitian (\blacklozenge), Eguiburu (\blacksquare), Tang (\blacksquare), polymerization (\blacksquare) and thermal degradation (\triangle) by Okamoto, Harshe used $\text{Ti}(\text{BuO})_4$ (\blacktriangle) and SnCl_2 (\blacktriangle) as catalysts, Rafler (\otimes).

by ROP, our polymerization conditions are suitable for on-site production.

The uncatalyzed polycondensation process did not give a higher PLA molecular weight. Because the dehydrative polycondensation of L-LA is driven by self-catalysis from L-LA's carboxyl group, the progress of the condensation decreases as the total amount of carboxyl group *in situ* is reduced by the polycondensation reaction [7,19]. Another reason for the generation of low Mw polymers is that the polycondensation process is carried out at moderate to high temperatures and under a strong vacuum, which not only allows for a fast reaction rate, but also aids in the removal of a small amount of the reactants [7].

The Mw/Mn ratio for PLA produced in uncatalyzed DP reactions varies from 2.0 to 3.2. On the other hand, this ratio is 1.5–3.77 for PLA produced by ROP [10,20,21], 1.4–5.5 for catalyzed DP [6,15,16,19,22,23] and 2.16–2.65 for uncatalyzed DP using D,L-lactic acid [15,16]. The ratio for DP was larger than that obtained by ROP, a process with a higher polymerization rate and a lower polymerization temperature than those in the present study. The broad range in the Mw/Mn ratio occurred because of intramolecular trans-esterification of the polymer chains that resulted in the formation of lactide and low Mw polymers [16,22,24]. These phenomena were caused by higher polymerization temperatures and longer polymerization times.

4.3. Activation and deactivation energies for the polymerization of polylactic acid

We compared the activation energy (E_a) of polymerization and the deactivation energy (E_d) of thermal degradation for the DP method with those of the ROP method. Fig. 5 shows the Arrhenius plot for polymerizations and thermal degradations under direct polycondensation and ring opening polymerization conditions. The polymerization rate constants k_2 and k_{app}^R were calculated from Eq. (10) for the DP method (present study) and from Eq. (14) for the ROP method, respectively.

$[A]_0$ in Eq. (4) is calculated using Eq. (20):

$$[A]_0 = \frac{\omega \times \rho}{M} \quad (20)$$

where ω is the monomer concentration, ρ is the density, and M is the initial molecular weight of L-LA. Propagation constants are plotted against the lefthand y-axis as solid lines in Fig. 5. However, the thermal degradation rate constants $k_{2\text{-app}}^D$ and k_{-1} were calcu-

Table 1

A comparison of the activation energy and deactivation energy for PLA polymerization.

Method	Material	Catalyst	Solvent	Temp. [°C]	Pressure (Vac./N ₂)	E _a [kJ/mol]	E _d [kJ/mol]	References
DP	L-LA	None	None	150–250	Vac.	50.46	38.49	Present work
				160–200	N ₂	31.03	–	
	D,L-LA	SnCl ₂	None	110–170	Vac.	56.64	–	[15] ^a
				110–180	Vac.	31.10	–	Harshe (2007)
ROP	D,L-Lactide	Aluminum/Schiff	Toluene	60–100	atm	23.6	–	[9]
				195–235	N ₂	15.10	–	[20] ^a
	L-Lactide	Titanium tetra isopropylate	None	80–110	N ₂	35.5	–	[11]
				120–220	N ₂	124	89.8	[12]
		Aluminum trialkoxides/ (2-methacryloxy)ethyloxy Tin octoate as catalyst and <i>n</i> -Dodecanohol as initiator						Okamoto (2008)

Vac: vacuum, atm: atmosphere.

^a E_a was calculated based on the data published by the authors quoted.

lated from Eq. (19) for the uncatalyzed reaction (present study) and from Eq. (17) in the case of the catalyzed reaction. Propagation constants are plotted against the righthand *y*-axis as dotted lines in Fig. 5.

The activation and deactivation energies were obtained from the slope of the Arrhenius plot. The results are summarized in Table 1, where the polymerization methods, materials, catalysts, solvents and operating conditions are included. It was found that the E_a for DP is generally larger than that of ROP. E_d is smaller than E_a for uncatalyzed DP conditions and these values agreed with the previous data for ROP [12].

4.4. Effect of temperature on the composition of condensate

The composition of the condensate during the distillation and oligomerization periods (*t* < 300 min) are shown in Fig. 6(a–d), plotted against polymerization temperature (T_p). They show the relationship of polymerization time (*t*) with the accumulated amount of water (a), monomeric lactic acid (b), low molecular weight oligomers, such as dimers, trimers and tetramers (c), and lactide (d) in Fig. 6(a–d), respectively. The total condensate is the

sum of these components, and was previously shown in Fig. 2. The amounts of each component were corrected for material loss in the flask and the condenser.

During the distillation period, the predominant component of the recovered material was water. During the oligomerization period, when pressure was incrementally reduced, monomeric lactic acid, oligomers, lactide and water were vaporized. At approximately *t* = 240 min, lactide began to condense in the trap, while polymerization proceeded in the reactor at all T_p until 5 h, as seen in Fig. 3. The lactide in the condenser was recovered and weighed. The growth process from monomeric lactic acid to oligomer agreed with the diagram by Vickroy [13]. The results showed that lactide is not directly made from lactic acid, but is produced from oligomers by cyclization.

Fig. 7 shows the proportion of each component in the condensate during polymerization and the PLA's degree of polymerization at 220 °C. At T_p = 220 °C, there was almost no change after oligomerization, except for lactide, which grew extraordinary until 30 h and then again after 53 h due to thermal degradation, the time when the PLA reached its maximum degree of polymerization (1140) in the reactor. Thus, these results show that lactide was produced from

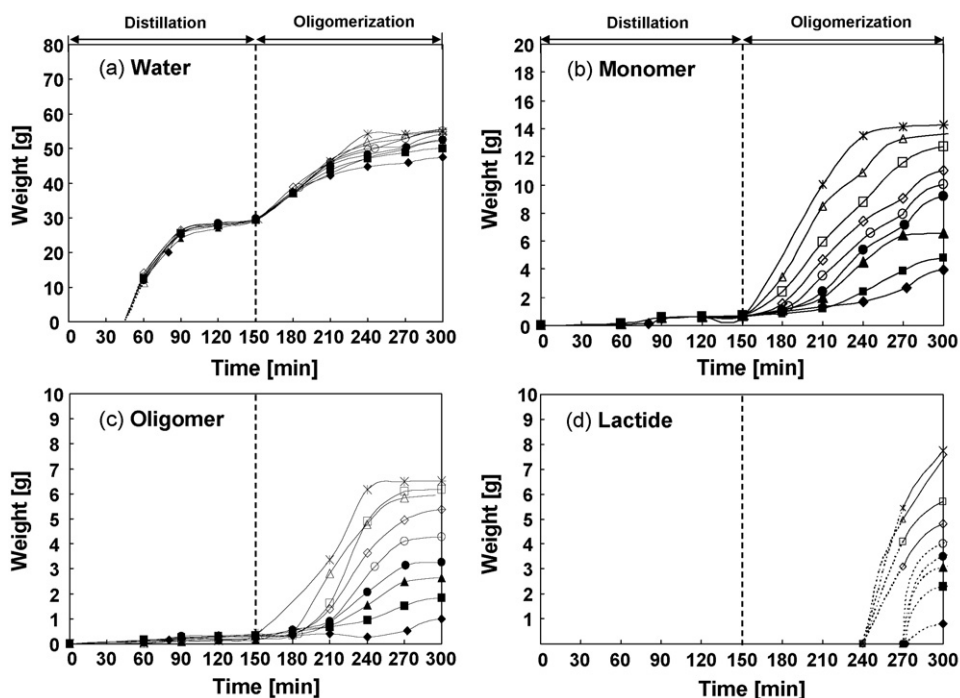


Fig. 6. The composition of the condensate during the distillation and oligomerization periods. Symbols: 150 °C (◆), 170 °C (■), 180 °C (▲), 190 °C (●), 200 °C (○), 210 °C (◇), 220 °C (□), 230 °C (△), 250 °C (*).

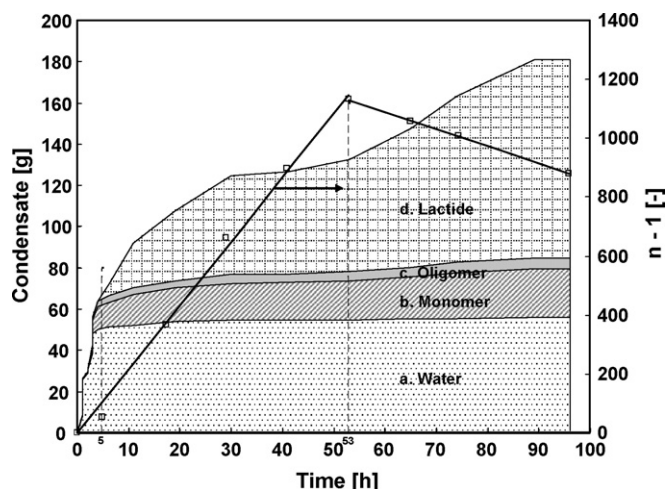


Fig. 7. The abundance of each component in the condensate during polymerization, and the degree of PLA polymerization at 220 °C.

the thermal degradation of PLA, and PLA showed a concomitant decrease in molecular weight [16,20,24].

4.5. The FTIR spectra of the products and starting material

The FTIR spectra of the products and starting materials are shown in Fig. 8. We compared the products in the reactor and condensate with standard materials. The FTIR spectrum of the raw material, lactic acid, is indicated by line (a). Lines (b) and (c) are of a lactide standard and products synthesized at 200 °C, respectively. Lines (d), (e) and (f) are FTIR spectra of PLA, with line (d) being the PLA standard, while lines (e) and (f) are the spectra of the PLA samples synthesized in this work. Lines (e) and (f) are spectra of PLA samples synthesized at 200 °C for 53 h, before thermal degradation (sample Q in Fig. 3b) and at 230 °C for 42 h, after thermal degradation (sample R in Fig. 3b), respectively. It is noteworthy

that the two samples' molecular weights were nearly identical ($M_w = 55$ kDa).

The polymer can undergo two forms of thermal degradation. One is the formation of lactide by cyclization, while the other involves the formation of a vinyl end group ($\text{CH}_2=\text{C}-$) by random scission, resulting in a peak at 1550 cm^{-1} in the FTIR spectrum [25]. It was found that the thermal degradation of PLA does not generate any vinyl end groups, but only occurs by the production of lactide, which is a raw material for the synthesis of PLA by ROP. Thus, we regard the lactide as a byproduct.

4.6. Mechanisms of polymerization and thermal degradation of PLA under uncatalyzed DP conditions

Fig. 9 shows the reaction mechanism for PLA formation. Water in the L-LA solution and that produced by self-esterification is removed by distillation at 150 °C. Subsequently, the L-LA forms oligomers with molecular weights in the range of 1000–5000 Da [5] (from Figs. 3 and 6), as shown in step 1 of Fig. 9. Lactide cannot be directly produced from L-LA because of the water in the reactor. The polymerizations proceed under vacuum to form low molecular weight PLA, as shown in step 2 of Fig. 9 (based on Fig. 7).

The thermal degradation of polymer chains forms smaller molecules, likely by specific scission to lactide (from Figs. 6 and 7) and did not form vinyl compounds by random scission (from Fig. 8).

Table 2 summarizes the yields for each polymerization temperature (T_p). We labeled the polylactic acid in the reactor as product I and the lactide in the condenser trap as product II. Final polymerization theoretically proceeds by the exclusion of one mole of water ($M = 18$) from one mole of lactic acid ($M = 90$). The net reactant mass was normalized by $(90 - 18)/90 = 0.8$. The yield of each product was then calculated by Eq. (21):

$$\text{yield (\%)} = \frac{\text{product [g]}}{\text{reactant [g]} \times 0.8} \times 100. \quad (21)$$

The yield of product I decreased with increasing polymerization temperature, while the yield of product II increased with increasing polymerization temperature and time. The total product yield

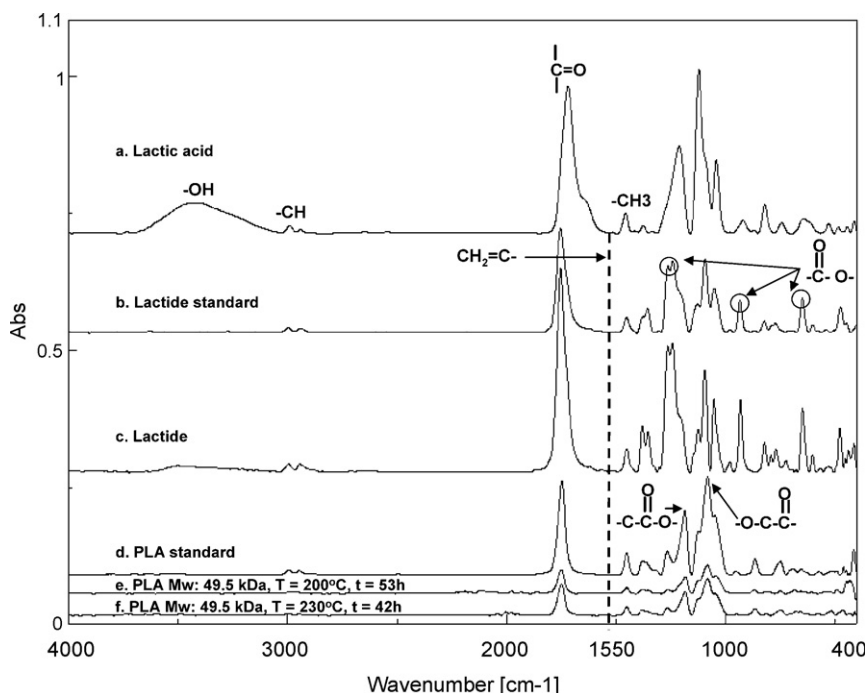


Fig. 8. The FTIR spectra of the products and starting materials.

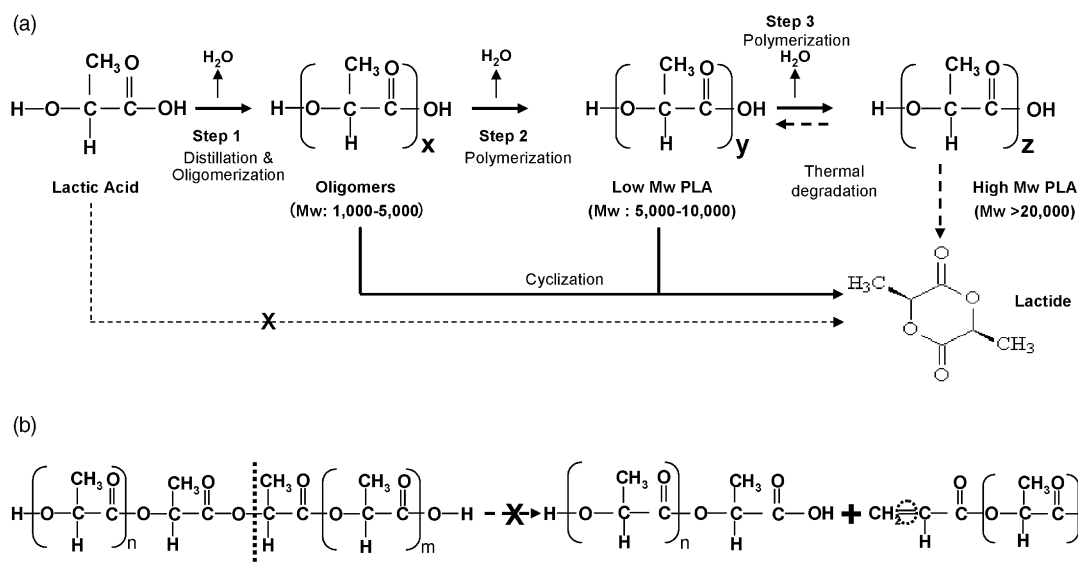


Fig. 9. Reaction mechanism for PLA polymerization and thermal degradation. (a) Polymerization and thermal degradation of PLA by specific scission. (b) Thermal degradation by random scission.

Table 2

The relationship between polymerization temperature and product yield.

T_p [°C]	Reactor		Condensate					Total yield [%]	
	Product I		Water [g]	Monomer [g]	Polymer [g]	Product II			Total [g]
	PLA [g]	Yield [%]				Lactide [g]	Yield [%]		
150	91.86	57.41	58.19	5.75	2.04	27.50	17.19	93.48	74.60
170	79.52	49.70	58.22	7.12	2.88	33.45	20.91	101.67	70.61
180	67.07	41.92	60.75	9.10	3.77	40.90	25.56	114.52	67.48
190	57.64	36.03	61.36	11.01	4.42	45.80	28.63	122.59	64.65
200	55.23	34.52	61.58	12.21	5.22	56.80	35.50	135.81	70.02
210	32.92	20.58	63.89	14.60	6.24	72.20	45.13	156.93	65.70
220	21.47	13.42	66.02	16.21	8.01	82.00	51.25	172.24	64.67
230	10.21	6.38	68.04	18.69	6.64	84.40	52.75	177.77	59.13
250	4.74	2.96	71.16	20.54	7.08	77.99	48.74	176.77	51.71

(the sum of products I and II) was in the range of 52–75 wt.%. The polymerization temperature should be restricted to the lower end of the range if product I is desired and should be limited to higher temperatures if product II is desired.

Bai and Lei [26] studied the effect of the amount of catalyst on the yield of PLA. They studied the synthesis of PLA from D,L-LA by DP using an organic carboxylic anhydride as a catalyst at 180 °C for 10 h under vacuum. The amount of each catalyst used in 20 mL LA was 0.3 g *cis*-butenedionic anhydride, 0.5 g phthalic anhydride and 0.3 g pyromellitic anhydride, which yielded 75, 78 and 79% yields of PLA, respectively, based on the pure D,L-LA. Furthermore, Takasu et al. have reported that the yield of PLA (based on the subtraction of the weight of the catalyst from the isolated material) is in the range of 5–60% for bulk polycondensation, and 73–90% for solution polycondensation of L-LA using Sc(OTf)₃ as a catalyst at 170 °C for 40 h and at 30 mmHg [22]. The low yield resulted from intramolecular trans-esterification (back-biting trans-esterification), which leads to the formation of the lactide [16,22,24].

5. Conclusion

Polymerization of L-LA by uncatalyzed direct polycondensation (DP) under vacuum was studied with the goal of adapting the method to on-site production. These experiments involved controlling only temperature and pressure. A second order phase transition occurred at 128 ± 2 °C, at which point the total acidity of L-LA was

enhanced to 100 wt.%. PLA reached a maximum molecular weight of 90 kDa at 200 °C under reduced pressure.

L-LA polymerization proceeds by a second order stepwise polycondensation. The activation energy for the uncatalyzed DP was greater than the activation energy for ring opening polymerization (ROP), which requires a catalyst. Thermal degradation occurred above 200 °C under reduced pressure. The deactivation energy for the thermal degradation reaction was also obtained from the Arrhenius plot. The deactivation energy was lower than the activation energy.

Thermal degradation by specific scission occurred above 200 °C in the DP method, which produced lactide, a starting material for ROP. The yield of the primary product (polylactic acid) decreased with increasing polymerization temperature, while the yield of the side product (lactide) increased with increasing polymerization temperature. The combined yield of PLA and lactide using this method ranged from 52 to 75 wt.%.

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